

**DETERMINATION OF HEAVY METAL CONCENTRATION IN TOP
SURFACE AND SUB SURFACE SOIL AROUND ULU TUALANG CLOSED
LANDFILL, TEMERLOH PAHANG**

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ABSTRACT

There are variety type of heavy metal may contain in the soil at the landfill. Heavy metal is the metallic chemical element that has a relatively high density and it is toxic and poisonous at low concentrations. The objectives of this research are to determine and analyses the distribution of heavy metal that present in the soil obtained from newly-closed landfill at Ulu Tualang Temerloh and to determine which heavy metal have higher amount of concentration in sub and top surfaces of the soil and also to compare it with the Environmental Protection Agency (EPA) Compost Standard. Heavy metal that will be analyses is zinc (Zn) and lead (Pb). For this experiment, after we pulverized and sieved the sample, we extract the sample using Acid Digestion Method, then both Zn and Pb concentration in the sample is determined using Atomic Absorption Spectroscopy (AAS). The result obtained is concentration of Pb in the soil is in range 5.65 mg/kg to 60.6 mg/kg while concentration range of Zn is between range 0.761 mg/kg to 16.365 mg/kg. As a conclusion, for overall the concentration of Pb is highest compared to Zn in top and sub surface of the soil and this heavy metal distribution data is under EPA Compost Standard (Zn and Pb) and also is very useful to be a good reference and guideline for soil remediation.

ABSTRAK

Terdapat pelbagai jenis logam berat yang mungkin terkandung di dalam tanah. Logam berat adalah unsur kimia logam yang mempunyai kepadatan relatif yang tinggi dan ianyatoksik dan beracun pada kepekatan rendah. Objektif kajian ini adalah untuk menentukan dan menganalisis pembahagian logam berat yang terkandung di dalam tanah yang diperolehi dari tempat pelupusan sampah di Ulu Tualang Temerloh dan untuk menentukan logam berat manakah yang mempunyai jumlah kepekatan yang lebih tinggi pada permukaan atas dan di dalam tanah serta untuk membandingkannya dengan Environmental Protection Agency (EPA) Kompos Standard. Logam berat yang akan analisis adalah Zink (Zn) dan Plumbum (Pb). Di dalam eksperimen ini, setelah sampel ditumbuk dan diayak, sampel kemudiannya diekstrak menggunakan kaedah Pencernaan Asid, seterusnya kepekatan Zn dan Pb di dalam sampel di tentukan denagn menggunakan Atomic Absorption Spektrometer (AAS). Keputusan yang diperoleh adalah konsentrasi Pb di dalam tanah adalah di dalam julat 5.65 mg/kg to 60.6 mg/kg manakala julat kepekatan Zn adalah antara 0.761 mg / L menjadi 16.365 mg / L. Sebagai kesimpulan, secara keseluruhannya kepekatan Pb lebih tinggi berbanding dengan Zn pada permukaan dan di dalam tanah dan data pembahagian logam berat ini adalah di bawah EPA Kompos Standard (Zn dan Pb) dan ianya juga sangat berguna untuk menjadi rujukan yang baik dan panduan untuk memperbaiki tanah.

TABLE OF CONTENTS

viii

CHAPTER	TITLE	PAGE
	DECLARATION	ii
	DEDICATION	iv
	ACKNOWLEDGEMENT	v
	ABSTRACT	vi
	ABSTRAK	vii
	TABLE OF CONTENTS	viii
	LIST OF TABLES	x
	LIST OF FIGURES	xi
	LIST OF APPENDICES	xii
	LIST OF ABBREVIATIONS	xiii
1	INTRODUCTION	
	1.1 Research background	
	1.2 Problem statement	1
	1.3 Objective	2
	1.4 Scope of study	2
	1.4.1 Area	3
	1.4.2 Soil Sample Region	3
	1.4.3 Type of Heavy Metal	4
	1.4.4 Method	4
		5

2	LITERATURE REVIEW	
	2.1 Introduction	6
	2.2 Effect of heavy metals	7
	2.3 Previous research / methodology	7
	2.4 Previous research / result and discussion	10
	2.5 Conclusion	13
3	METHODOLOGY	
	3.1 Procedure	17
	3.2 Equipment/apparatus/material	20
	3.3 Reagents	20
	3.4 Preparation of standard curve	21
	3.5 AAS spike method	22
	3.6 Summary of Leads and Zinc Sample Analysis	23
4	RESULTS AND DISCUSSIONS	
	4.1 Introduction	24
	4.2 Spike 5 ppm method	27
	4.3 Lead	28
	4.4 Zinc	30
	4.5 Discussion	33
	CONCLUSION AND RECOMMENDATION	
5	5.1 Conclusion	40
	5.2 Recommendation	41
	REFERENCES	42
	APPENDICES	45

LIST OF TABLES

Table 2.1	Comparison of leachate quality of Kuwait (Al-Sulaybiya) with other leachates reported for developed countries	10
Table 2.2	Summary of statistics of heavy metal that done in Chennai India	12
Table 2.3	Information of zinc	14
Table 2.4	Information of lead	15
Table 2.5	Properties of Zinc and Lead	16
Table 4.1	Lead (Pb) reading by AAS after Spike Method	28
Table 4.2	Lead concentration data	29
Table 4.3	Zinc (Zn) reading by AAS	30
Table 4.4	Zinc concentration data	31
Table 4.5	Summary of Lead and Zinc Concentration Data	37
Table 4.6	pH values for top soil and sub surface soil	38
Table 4.7	Type of soil	38

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
1.1	Ulu Tualang closed landfill map	3
3.1	Sampling Point Gridding Area	18
3.2	Standard solution of zinc, Zn	21
4.1	Sampling Point Gridding Area	25
4.2	Sample Collecting	26
4.3	Graph of Pb concentration vs sampling point	28
4.4	Graph of Zn concentration vs sampling point	31
4.5	Graph of heavy metal concentration vs sampling point in top surface soil	33
4.6	Graph of heavy metal concentration vs sampling point in sub surface soil	33
4.7	Ulu Tualang Closed Landfill physical properties	34
4.8	3-D Graph to show distribution of lead in top surface soil	35
4.9	3-D Graph to show distribution of lead in sub surface soil	35
4.10	3-D Graph to show distribution of zinc in top surface soil	36
4.11	3-D Graph to show distribution of zinc in sub surface soil	36

LIST OF APPENDICES

NAME	TITLE	PAGE
Figure A.1	Ulu Tualang Landfill	46
Figure A.2	Collected Samples	46
Figure A.3	Sample (Lump form)	47
Figure A.4	Sample (Powder form)	47
Figure A.5	Digestion Stage	47
Figure A.6	Sample (Liquid form)	47
Figure A.7	Standard solution of zinc, Zn and lead, Pb	48
Figure A.8	Atomic Adsorption Spectrometer (AAS)	48
Table A.1	Lead (Pb) reading in ppm at first test	49
Table A.2	Lead (Pb) reading in ppm after 5 ppm spike method	50
Table A.3	Zinc (Zn) reading in ppm at first test	51

LIST OF ABBREVIATIONS

AAS	- Atomic Adsorption Spectrometer
Zn	- Zinc
HCL	- Hydrochloric Acid
Ppm	- Part per million
HNO ₃	- Nitric Acid
Cr	- Chromium
Cu	- Cuprum
Pb	- Lead
M	- Concentration
V	- Volume
EPA	- Environmental Protection Agency
MSW	- Municipal Solid Waste
HWL	- Hazardous Waste Landfill
PCDD/Fs	- polychlorinated dibenzo-p-dioxins and dibenzofurans
Cd	- Cadmium
Cr	- Chromium
Cu	- Copper
Ni	- Nickel
Fe	- Ferum
Mn	- Manganese
Al	- Aluminum

B	- Barium
K	- Pottasium
Na	- Natrium
BOD	- Bio-oxygen demand
COD	- Chemical oxygen demand
TCLP	- Toxicity Characteristics Leaching Procedure
Hg	- Mercury
As	- Arsenic
USEPA	- United State Environmental Agency Protection
OM	- Organic Matter
NAA	- Neutron Activation Analysis
NO ₂	- Nitrous Dioxide
EU PEL	- European permissible exposure limit
CCME	- Canadian Council of Ministers of the Environment

CHAPTER 1

INTRODUCTION

1.1 Research Background

Nowadays landfill has accepted as a reasonable and widely useful technology that uses at most of developing country. Beside it can accommodate large amount of waste disposal, it also give low investment and operational cost (Chai Xiaoli *et al.*, 2007). But for a certain time, landfill also is a major factor that gives bad effect to the environmental pollution. The soil at the landfill may become toxic and poison because of presence of higher concentration of heavy metal (M.S Li *et al.*, (2007)). Even though there is some metal that good to the soil which is may come from dumping waste, (such as nitrate that can act as fertilizer to the soil), but most of the soil will accepted more type of dangerous heavy metal in the soil that will lead to the negative effects. This situation will make the soil have more dangerous and toxic heavy metal rather than good heavy metal.

After a long time, waste that decomposed at the landfill will make the soil become polluted and may contain large amount of heavy metal. There are some of heavy metal can react with rain rich oxygen to form sulphur and then produces macromolecule of sulphides. These hazardous molecules will influences the quality of atmosphere thus may affect health and life of animal and human being that closed to the landfill. Usually after the landfill is closed, that placed is usually reconstructed as recreational places or residential area. A lot of problems will occur if the soil becomes porous and not stable

because of the presence of heavy metal in the soil. Even though there are some heavy metal that may good for the soil, but most of heavy metal that come from industrial waste are toxic and dangerous to human. This issues then will make the reconstructed area are not safe and not suitable for human lives.

1.2 Problem Statement

The dangerous possibility may occur such as contamination of the crop (in term of heavy metal uptake by the plant), pollution of underground water, influence the plant growth and make the soil generally considered toxic(Peter Ryser *et al.*, 2006). In agricultural activity, if the soil that contains a large amount of heavy metal is used, the plant cannot grow well and may be intoxicated. It will affect the health of the human or animal when they took the plants as their meals. The critical issues mentioned above should be avoided to make sure that if the soil is used for human activity, it must be safe and not contain toxic heavy metal that may dangerous and would lead to environmental pollution.

1.3 Objectives

The objectives of this result are:

- I. Determine and analyses distribution of heavy metal that present in the soil cause by decomposition of waste in the landfill
- II. Determine which heavy metal have higher amount of concentration in sub surfaces and top of the soil

1.4 Scope of Study

1.4.1 Area

For this study, the soil sample that use is from closed landfill at Kampung Ulu Tualang Temerloh, Pahang. This landfill is near to the Temerloh Industrial Estate and Mentakab Industrial Park that focusing in stainless steel fabrication and wood base industry.



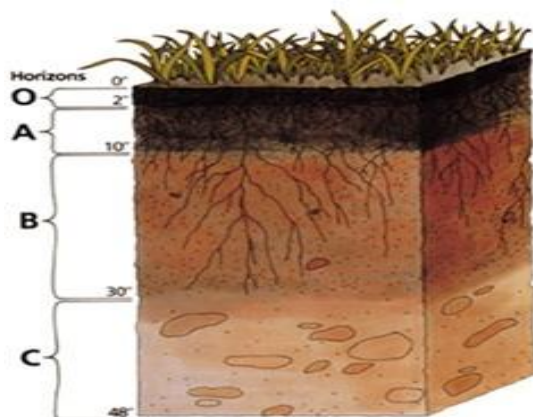
Figure 1.1: Ulu Tualang closed landfill map

The company list that probably using the landfill ;

- i. SQ Wooden Picture Frame Moulding Sdn Bhd (Picture Frames - Wholesaler & Manufacturers).
- ii. Mentakab Stainless Steel Works (Stainless Steel Fabricators).
- iii. Syarikat Perniagaan Boon Wee (Biscuits - Wholesaler & Manufacturers, Food Products).
- iv. Megaply Industries (M) Sdn Bhd (Plywood & Veneers).
- v. Intan Suria Sdn Bhd (Frames - Picture, Wood Products).
- vi. Mentakab Agricultural Machinery Sdn Bhd (Agricultural Equipment & Supplies, Tractor Distributors & Manufacturers).
- vii. LCS Precast Sdn Bhd (Piling).

1.4.2 Soil Sample Region

- Soil sample are taken at O and A region



Region A = within depth 2-10 inch

Region B = within depth 10 – 30 inch

1.4.3 Type of Heavy Metal

- Lead is a bluish-white lustrous metal. It is very soft, highly malleable, ductile, and a relatively poor conductor of electricity. It is very resistant to corrosion but tarnishes upon exposure to air. Lead isotopes are the end products of each of the three series of naturally occurring radioactive elements.
- Zinc is a lustrous bluish-white metal. It is found in group IIb of the periodic table. It is brittle and crystalline at ordinary temperatures, but it becomes ductile and malleable when heated between 110°C and 150°C. It is a fairly reactive metal that will combine with oxygen and other non-metals, and will react with dilute acids to release hydrogen.

1.4.4 Method

In this experiment, we divide the experiment into three phases which is sampling and pre-treatment stage, sample digestion or extraction stage using Acid Digestion Method and analysis of the sample by using Atomic Absorption Spectrometer (AAS) in order to determine the concentration of heavy metal in plant and also soil.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Nowadays there are many developing countries that use landfill to provide a place for waste disposal management. A research done by Chai Xiaoli *et al.*, (2007), it shows that more than 90% refused are disposed in landfill at China but this developing country has recently closed more than 1000 landfills because of environmental concern. An example from Chai Xiaoli *et al.*, (2007) research, they state that after the largest landfill in China, Shanghai Laogang Refuse Landfill that constructed in 1985 along the shore of the East China Sea was closed after handling and treats about 30 million tones of refused up to 2005, they preferred Municipal Solid Waste (MSW) landfill to replaced previous landfill because of its offers potential economic benefits by creates additional disposal capacity for the placement of fresh refuse, and recycles the stabilized, valuable resource. This is important for promoting the sustainable environmental development of a society. But before the reclamation of a landfill can be implemented and the residues can be reused outside the landfill environment, it is necessary to comprehensively characterize heavy metals in the landfill. By analyzing heavy metal content in soil reclaimed from an MSW landfill, we can assess the possible limitation of reuse of the reclaimed soil in the landfill and also avoid the environmental pollution effect that may comes because of heavy metal contamination in that soil .

2.2 Effect of Heavy Metals

A research done by M.S Li *et al.*, (2007) also done in China, large amount of heavy metal also found in Guangxi, South China cause by mining process and decomposition of coal in landfill soil. Mining, in particular the metal ore extraction is the second source of heavy metal (especially manganese) contamination in soil after sewage sludge. Even though there are some perception that told manganese are non-toxic metal element, but the fact is exposure too much to manganese may cause health damage such as Parkinson-like symptoms. Manganese ore also can accompany with other heavy metal mixture such as Pb, Zn, Cd, Ni, Co and Fe and extraction of this combine element will lead to release of more toxic metals into the environment.

2.3 Previous Research / Methodology

In Catalonia, Spain, in Montse Mari *et al.*, (2009) research, they collect information from European Commission and found that 1.3 billion tons of waste including 36 million tonnes hazardous waste was produced there. It may come from different origins such as households, commercial activities and industry and they must be properly managed to minimize their impact on the environment and human health. Their research was done in Castellolí (Barcelona Province, Catalonia) and this place is classified as class III hazardous waste landfill (HWL). Heavy metal contained there may come from hazardous material such as municipal waste incinerator fly ashes, asbestos, as well as other inert wastes. Fly ashes are characterized by a high content of heavy metals and organic compounds such as polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs). In their research, they concern about the human risk health that been living around the HWL area so that they analyze soil and air condition at the landfill. They found relatively higher concentrations of PCDD/Fs, as well as some metals such as Pb, in soil samples of the HWL of Castellolí and also soil samples at the villages located in the vicinity than in those obtained in samples collected from the other places. So that they finally conclude this HWL area is not safe for human population but in term of

environmental issue, this pollution matter should be monitored well in order to avoid contamination happen there will not experiencing and show an increasing trend.

In this new millennium world, there are more research and technique that use to study and analyze presence of heavy metal in the soil. In a research done by A.Kasassi *et al.*, (2008), they found that extensive and long industrial operation that done in landfill site at Efkarpia, Thessaloniki gave higher concentration amount of toxic and dangerous heavy metal to the soil which is cadmium (Cd), chromium (Cr), copper (Cu,) nickel (Ni), lead (Pb) and zinc (Zn). Most of the soil is obtained from deeper site of the landfill, it shows that the waste is decomposed for a long time and it reaches the deeper site in the soil. The higher value of heavy metal found is in depth over 2.5 m. The soil samples collected from this area, which is one of the largest industrial areas where metal-processing, chemical, furniture and wood, textiles and clothing, food, chemical and cement industries are located there. The related produced wastes are 240, 220, 200, 150, 110 and 40 tons/year respectively. For the method to collect and prepared the samples, they drill the site in range of 2.5 m to 17.5 m. Then all samples were stored in a covered place and left to dry out. They were pulverized and sorted all the samples with a 2-mm sieve. For the extraction method, 2 g of each pulverized sample were weighed and placed in conical bottles of 100 or 200 mL. After the addition of 25 mL of HNO₃ 4 M, the bottle was placed in a sand bath; funnels with filters were placed in the neck of the bottle, in order for the digestion to take place under constant volume. The solution was heated in 70 – 80 °C for 16 h. After heating, the sample was filtered in a volumetric bottle of 50 mL. Finally, the bottle was filled up to the slit with deionized water. The samples were refrigerated for maintenance (4 °C). This method was applied to all 40 samples as well and finally analyzed by Atomic Absorption Spectrometer (AAS).

Same thing state by research of M. Ostman *et al.*, (2006), they found that heavy metal at Sweden landfill are dissolved as organic metal and it transported to downward of the landfill. The landfill studied is situated at Hogbytorp, 40 km northwest of Stockholm, Sweden. Wastes that come to this landfill can be classified into five main classes; building and construction waste, household waste, sludge, filling material (inert

material) and also ash and slags. This landfill starts its operation in 1964 and the closure is estimated to be in 2005, when the wastes contain approximately 4 million tons of waste. From its starting operation at 1964 to the beginning of 1983 the major proportion of the waste was household waste, but from 1984 building and construction waste began to dominate the waste. For the collecting the samples in this landfill site, they drilled the landfill until depth of 18 m. Then all the samples have been drying follow next steps which is by crushing and sieving. Larger metal items were removed from the sample including gravel and stones. The samples then were carefully mixed. For the analyses of heavy metals, all samples were extracted using nitric acid soluble speciation, which was chosen to get an estimate of the metal content as near as possible to the total content in the material. Silicate minerals are not soluble in nitric acid, so for Al, B, K and Na only a small amount of the total content was dissolved in the nitric acid, but for the rest of the elements analyzed, approximately about 70–90% of total content was obtained. At the end of their research, they confirm and conclude that soils from this landfill area contain large number of heavy metals. This condition makes the stability of the landfill difficult to predict. Furthermore, they also assumed that some of the metals can bound with sulphur element and other organic materials in the macromolecules. When it reacts with oxygen-rain water, these elements will release from both organic material and sulphides which is a very hazardous material. It then makes the area of the landfill and nearest area there polluted, did not safe for living and this environmental issue must be handled well regard to the fate of metals present there.

Most of the researcher has done drilling method in order to take the sample. In a research done by L. Borgna *et al.*, (2009), they take sample from top surface of the soil until depth of 20cm. For the extraction method, we use acid digestion of sediments, sludge's, and soils method. This method is a very strong acid digestion method that will dissolve almost of elements that could become environmentally available. It also doesn't have higher operation cost. The need for accurate and precise analyses of toxic metals is becoming an important aspect, as we learn more about their behavior and causes if they're in the environment and in the food chain. The harmful effects of many of these metals to man and nature are well known while the number of elements that to be determined

continues to increase, and also in a demand for low detection limits. According to research done by Timo Myöhänen *et al.*, (2002), they use another type of digestion method which is aqua-regia digestion method. This method is quite popular method that always uses to determine concentration of heavy metal., aqua-regia method give shorten time for analyzing method. But, in term of precision, it cannot determine concentration of heavy metal accurately if we want proceed to last method using atomic absorption spectroscopy (AAS).

2.4 Previous Research / Result and Discussion

In a research done by A.F Al-Yaqout *et al.*, (2003), they compared the soil contamination at the leachate landfill from developed country which is USA, Germany and Italy in term of amount of pH, bio-oxygen demand (BOD), chemical oxygen demand (COD) and distribution of heavy metal with their country.

Table 2.1: Comparison of leachate quality of Kuwait (Al-Sulaybiya) with other leachates reported for developed countries

Parameter (mg/l)	Kuwait	USA	Italy	Germany
Alkalinity (as CaCO ₃)	250–6340	240– 8965	4250– 8250	-
pH	6.9– 8.2	5.1–6.9	6.0–8.5	5.7– 8.1
BOD	30– 600	13,400	2125– 10,400	400–45,900
COD	157.9–9440	1340– 18,100	7750– 38,520	1630–63,700
Sulfate	55– 3650	0.01– 1280	219–1860	1– 121
Zn	0.0– 4.8	18.8– 67	5 – 7	-
Pb	0– 0.2	0 –4.46	–	–
Cu	0– 0.2	0 –0.1	–	–
Fe	0.3– 54.1	4.2–1185	47–330	8– 79
Ca	5.6– 122	254.1– 2300	0 – 175	70– 290
Mg	5.2– 268	233– 410	827–1469	100–270

From the table, it show that developed country produce higher amount of heavy metal thus lead to more environmental pollution. This is due to the amount of waste produce is higher from this four developing country.

The Ulu Tualang closed landfill gets most of waste disposal similiar with research done by S. Esakku *et al.*, (2003). The dumping site at Chennai India get the unused waste about 3500 tons/day such as electronic goods, electro plating waste, painting waste, used batteries and this various waste sources may come from developed such as USA, Singapore and South Korea. It will lead to the environmental issue matter if unorganized dumping of solid waste management authorized there. It also will cause serious health damaged due to the released of toxic heavy material that comes from this landfill. People that exposed to this environment can be affected to their health such as blood and bones disorder, kidney damage, decreased of mental capacity and also damage the neurological systems. In their research, for solid waste sampling procedures, they drilled about 3m depth in the landfill to get the sample. The sample then was analyzed by using water extract method, Toxicity Characteristics Leaching Procedure (TCLP) and also aqua regia acid digestion method. As a result, they found that the soil have higher concentration of zinc compare than other heavy metals (Hg, As, Cd, Ni, Pb, Cu and Cr) and the heavy metal distribution was found most at top surface of the soil within depth 1-2 meter. The summary of the distribution data can be explained in Table 2.1.

Table 2.2: Summary of statistics of heavy metal that done in Chennai India

S.No	Particulars	Hg	As	Cd	Ni	Pb	Cu	Cr	Zn
1	Minimum	0.039	0.077	0.820	21.0	53.0	75.0	110.0	167.0
2	Maximum	0.78	1.561	1.77	50.0	112.0	217.0	261.0	503.0
3	Median	0.21	0.451	1.28	33	85	105	129.5	230.5
4	Mean \pm SD	0.29 \pm 0.22	0.57 \pm 0.38	1.29 \pm 0.31	32 \pm 8	86 \pm 16	113 \pm 42	140 \pm 40	284 \pm 111
5	Indian Compost Standards *	0.15	10.0	5.0	50	100	300	50	1000
6	USEPA Compost Standards **	17.0	41.0	39.0	420	300	1500	1200	2800

All the values are in mg/kg. No. of samples: 12

* MSW (Management and Handling) Rules, 2000.

** US Composting Council, 1997.

From the table, we can see that from their research heavy metals that was found did exceed the India Compost Standard but when comparing with United State Environmental Agency Protection (USEPA) standard, all are them is within the standard limits. Another research done by Abdelatif Mukhtar Ahmed *et al.*, (2001), they compared the concentration of heavy metal that found in Seri Petaling landfill with USA, Poland and China landfill. According to them, concentration of heavy metal in landfill at Malaysia is quite low compare than the other country. It proves that as a developing country, Malaysia produced less waste disposal compare than the other 1st World Country. Besides that, a research done also in Malaysia done by Md. Mizanur Rahman *et al.*, (1997), they found that industrial places such as Taman Beringin landfill produced more waste disposal then lead to decomposition of variable heavy metals in the soil compare than the other places.

Heavy metal accumulation in soils makes the soils becomes loss of its functions then leading to concerns about environmental quality protection, maintenance of human health and productivity. Soil pollution can have implications in phytotoxicity at high concentrations and as a result in the transfer of heavy metals to the human diet from crop uptake or soil ingestion by grazing livestock. A research done at Yocsina, Córdoba Province Argentina by Gonzalo M.A. Bermudez *et al.*, (2009), they studied about soil located near to the cement plant. Cement plants are important emission sources of pollution of both organic and inorganic chemicals, and it produce a large number of

metals and metalloids elements such as As, Cd, Ca, Co, Cr, Cu, Ni, Pb and Zn. They top surface soil sample was collected within the depth 0 – 10 cm in 25 meter per square and within this gridding area, nine sub soil samples were randomly chosen. All the samples then were analyzed to determine pH value, organic matter (OM) content and also distribution of heavy metal analysis done by Neutron Activation Analysis (NAA) after extracted by 0.5 M HCl-extractable heavy metals method. This method has been successfully used to get the total non-residual or non-latticeheld heavy metal concentrations in streams, road sediments and also in soils. As a result, they found that most of the heavy metal contains in the soil at the cement plant there and people that live near to this cement plant have high risk to expose to the toxicity of dangerous affects of heavy metal such as Ba and Cr that highly detected in this plant.

2.5 Conclusion

Although the previous literature gave a lot of experimental data with variable technique done, it still has a room to make an improvement in order to achieve perfectness. Data that will be obtained can be more precise and accurate because of latest technology compare to their time. This important aspect should be done continuously time by time so that we can always alert to the dangerous possibility that may comes from the waste dumping site. Therefore, another research study about presence of heavy metal and their quantity in the soil should be done to avoid any unexpected thing that may happen.

In this study, statistical data can be plotted and it will be very useful for landfills treatment and become references for the land developer when they start to reconstruct this closed landfill. Decomposition of this heavy metal may lead to more good effect or vice versa to human lives near to the landfill. It can act either good for fertilizer to the soil or leads to more bad effect that cause environmental pollution. When the soil is detected contain large amount of heavy metal that totally dangerous and contain higher toxicity, it is important to us to make that the soil safe first before reconstructed it for human activity there to avoid any unexpected incident occur.

Table 2.3: Information of zinc



<p>General information</p> 	<ul style="list-style-type: none"> - Lustrous bluish-white metal - brittle and crystalline at ordinary temperatures, but it becomes ductile and malleable when heated between 110°C and 150°C - Reactive metal that will combine with oxygen and other non-metals, it will react with dilute acids to release hydrogen
<p>Application</p>	<ul style="list-style-type: none"> - Always used in principally for galvanizing iron, in the preparation of certain alloys, used for the negative plates in some electric batteries and for roofing and gutters in building construction, used in die casting in the automobile industry - White pigment (zinc oxide) - used in plastics, cosmetics, photocopier paper, wallpaper, printing inks - Can also act as catalyst during manufacture and as a heat disperser in the final product in rubber production
<p>Health effects of zinc</p>	<ul style="list-style-type: none"> - can experience a loss of appetite, decreased sense of taste and smell, slow wound healing and skin sores - cause birth defects - high amount of zinc can cause stomach cramps, skin irritations, vomiting, nausea, anemia, damage the pancreas, disturb the protein metabolism and can cause respiratory disorders
<p>Environmental effects of zinc</p>	<ul style="list-style-type: none"> - increase the acidity of waters - Water-soluble zinc that is located in soils can contaminate groundwater - Decrease the plant survival chances - Interrupts activity of microorganisms in soils

Table 2.4: Information of lead

<p>General information</p> 	<ul style="list-style-type: none"> - bluish-white lustrous metal - very soft, highly malleable, ductile - poor conductor of electricity - a radioactive elements
<p>Application</p>	<ul style="list-style-type: none"> - used in piping systems - constituent of the lead-acid battery used extensively in car batteries - used as a coloring element in ceramic glazes - commonly uses is in the glass of computer and television screens, where it shields the viewer from radiation - Other uses - in sheeting, cables, solders, lead crystal glassware, ammunitions, bearings and as weight in sport equipment
<p>Health effects of lead</p>	<ul style="list-style-type: none"> - Disruption of the biosynthesis of hemoglobin and anemia, a rise in blood pressure, kidney damage, disruption of nervous systems, brain damage - Declined fertility of men through sperm damage - Diminished learning abilities of children - Behavioral disruptions of children, such as aggression, impulsive behavior and hyperactivity
<p>Environmental effects of lead</p>	<ul style="list-style-type: none"> - increase the acidity of waters in corrosive pipe - disturb the soil functions by lead intervention - poison the water and soil organisms